

PATENT ABSTRACTS OF JAPAN

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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a high capacity and long life characteristics showing an electrolyte quantity that is suitable for a high density battery with few gaps by defining the electrolyte quantity and the concentration of lithium salt contained in it.

SOLUTION: When the total electrolyte quantity in the battery is made Q the non-aqueous electrolyte satisfies the formula $(Vx + 0.4Vy) \leq Q \leq (Vx + 0.8Vy)$. Wherein Vx represents the total holes of a positive electrode made of positive electrode active substance comprising mainly lithium cobalt oxide and negative electrode

made of negative electrode active substance comprising mainly graphite and a polymer membrane and V_y represents the space between the electrodes and the polymer membrane the space between the side face of a group made of the electrodes and the polymer membrane and the inner wall of the battery case and the gaps inside the battery (upper part and lower part of the group).

CLAIMS

[Claim(s)]

[Claim 1] An anode which uses a lithium cobalt oxide characterized by comprising the following as main positive active material It has a negative electrode which used natural graphite or an artificial graphite as main negative electrode active material a porous poly membrane arranged among them and nonaqueous electrolyte and volume capacity density is a lithium secondary battery of 400 or more Wh/L.

When said nonaqueous electrolyte sets the all amount of electrolysis solutions in a cell to Q_Q is said anode said negative electrode and all the holes V_x of said poly membrane.

Space and said electrode and said poly membrane between said electrode and said poly membrane.

***** -- a lithium secondary battery characterized by things.

[Claim 2] Volume of V_2 and said poly membrane is set [volume of said anode] to V_3 for volume of V_1 and said negative electrode When a void content of beta 2 and said poly membrane is set [a void content of said anode] to beta 3 for a void content of beta 1 and said negative electrode The lithium secondary battery according to claim 1 wherein the group space volume V_x which is said anode said negative electrode and the total hole volume of said poly membrane was calculated by $V_x = V_1\beta_1 + V_2\beta_2 + V_3\beta_3$ and said electrolysis solution has permeated said group space volume V_x .

[Claim 3]The lithium secondary battery according to claim 2 characterized by Vg occupying not less than 90% of cell inner space when volume also including a hole of a group of electrode is set to Vg.

[Claim 4]The void content beta 1 of said anode and the void content beta 2 of said negative electrode with the mercury porosimeter. The lithium secondary battery according to claim 2 with which it is not less than 10% of 50% or less in a measured value and the void content beta 3 of said poly membrane is characterized by being 50% or less not less than 30% with a value measured by the mercury porosimeter.

[Claim 5]Space between said electrode and said poly membrane and between the group side and a cell case wall and the opening Vy in a cell (the upper part and the lower part of a group)The lithium secondary battery according to claim 1 characterized by being $Vy=V_{cell}-V_g-****$ when volume of a lead which is a member which considers it as the cell inner space V_{cell} and exists in a cell tape and a frame is set to ****.

[Claim 6]The lithium secondary battery according to any one of claims 1 to 5 whose angle of contact theta over said anode and negative electrode and a polymers membrane surface viscosity of said electrolysis solution is 5 or less cp of 0.5 or more cp and is $0 < \theta < 80$ degrees.

[Claim 7]The lithium secondary battery according to claim 6 with which lithium salt which is dissolving into a solvent of said electrolysis solution is characterized by 0.5 or more mol/l being 2.0 or less mol/l.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]In this invention the distributing quantity and the characteristic of the electrolysis solution in a cell of a lithium secondary battery

are made suitable.

Therefore it is related with the high capacity-ized lithium secondary battery which has improved the battery characteristics especially the cycle characteristic.

[0002]

[Description of the Prior Art] The charging and discharging characteristic and cycle characteristic of a lithium secondary battery are greatly influenced by the active material kind of an anode and a negative electrode the electrolysis solution kind etc. and serve as combination of an anode and a negative electrode the amount of electrolysis solutions of an electrolysis solution and an element with an important relation of an opening etc. further.

[0003] Obtaining the lithium secondary battery which has the charging and discharging characteristic outstanding by specifying the amount of electrolysis solutions per cell capacity 1Ah and constituting a cell as volume regulation of the electrolysis solution in a lithium secondary battery is proposed (JP9-231973AJP2000-285959Aetc.).

[0004] By specifying the amount of electrolysis solutions per cell inner volume and using the high separator of an electrolyte holding rate in a laminate type battery In order to lessen the rate of the electrolysis solution which exists in the free state (state which has not permeated the anode negative electrode and separator which are power generation elements) where it does not participate in a power generation element and to press down a liquid spill of the electrolysis solution by the rise of inter cell pressure The liquid electrolyte holding rate of a separator is carried out in cc and not less than 1.5g / and the composition which constitutes a cell from 0.2 cc or more less than 0.4 cc is also proposed in the amount of electrolysis solutions per cell inner volume (JP7-282818A).

[0005] In order to control the internal pressure rise of gas to prevent a liquid spill cell breakage etc. by an internal pressure rise in the lithium secondary battery using the negative electrode which consists of an organic baking body to be long lasting and to make it a highly reliable cell Providing a cavity part of 0.3 cc [per

capacity 1Ah] or more in a container is proposed (the patent No. 2646657 gazette).

[0006]In order to stop the amount of consumption of lithium and to control capacity deterioration in the nonaqueous electrolyte secondary battery using the anode which becomes others from a lithium manganic acid ghostWhen total of the volume of voids calculated from an anodea negative electrodeand the voidage of each separator is set to 1it is proposed that the volume of the nonaqueous electrolyte uses 0.8-1.5 (JP2000-294294A).

[0007]

[Problem(s) to be Solved by the Invention]High capacity-ization of a lithium secondary battery progresses and research and development of the cell by which volume capacity density exceeds 400 Wh/L are furthered these days.

[0008]As one of the art of high-capacity-izing of this cellstuffing a power generation element into the densification and cell inner volume of a mixture in a polar plate as much as possible is advanced. In this caseit is necessary to lessen space used as the power generation element per capacity as much as possibleand the voidage in a group of electrode is also small.

[0009]Thusin the methods (JP9-231973AJP2000-285959Aetc.) of prescribing the volume per capacity that the voidage in a group of electrode becomes smallthe free liquid which does not participate in charge and discharge increases in numberand it is not suitable for high capacity-ization.

[0010]on the contrarythe thing which has a void content thin a separator and low in a high capacity-ized cell although the proposal which abolishes a free state by using the separator of a high electrolyte holding rate for JP7-282818A like the composition of a statement is also made -- not using -- it cannot obtain and apply.

[0011]The composition which provides a cavity part of 0.3 cc [per capacity 1Ah] or more in a container given in the patent No. 2646657 gazette is effective when a negative electrode is an organic baking bodybut. a high capacity-ized cell -- negative electrode active material -- a high-capacity-izing sake -- material of a black lead system with small irreversible capacity -- not using -- it cannot obtain

and apply.

[0012]When total of the volume of voids calculated from an anode given in JP2000-294294Aa negative electrodeand the voidage of each separator is set to 1When an anode consists of a lithium manganic acid ghostthe composition which the volume of the nonaqueous electrolyte sets to 0.8-1.5 is effective in order to stop the amount of consumption of lithium and to control capacity deteriorationbut. a lithium cobalt oxide also with discharge voltage high [positive active material] because of high-capacity-izingand weight energy density high in a high capacity-ized cell -- not using -- it cannot obtain and apply.

[0013]Thusare the optimal viscosity for the hole in the anode and negative electrode which are the power generation elements in a celland a poly membraneand the space between an electrode and a poly membranethe optimal electrolysis solution was made to permeateand the technical problem that the art which constitutes the amount of electrolysis solutions optimal in a cell was not enough occurred.

[0014]As mentioned abovethis invention solves such a technical problem and it aims at securing the high capacity and the high lifetime of few lithium secondary batteries of an openingWhen an electrolysis solution fills the opening in an anodea negative electrodeand a poly membraneand the space between the poly membranes used as an electrode and a separator the optimallon conductivity of the lithium ion between a polar plate and the poly membrane in a polar plate can be made goodand the lithium secondary battery which can carry out the maximum use of the positive active material and negative electrode active material which are power generation elements can be provided.

[0015]

[Means for Solving the Problem]To achieve the above objectsa lithium secondary battery of this inventionWhen the all amount of electrolysis solutions in a cell is set to Q in said nonaqueous electrolyteQ Said anodesaid negative electrodeand all the holes Vx of said poly membranelt is expressed by space between the side of a group of electrode and a cell case wall which consist of between said

electrode and said poly membrane and said electrodeand said poly membraneand the opening Vy in a cell (the upper part and the lower part of a group)and is $\leq (Vx+0.4Vy)$ $Q \leq (Vx+0.8Vy)$.

***** -- it is characterized by things.

[0016]By thingshigh capacity and a high lifetime lithium secondary battery can be obtained making composition of an invention be the above. Even when an electrode group expands by repetition of charge and discharge in a cell of this inventionin order that there may be no ***** and there may be no liquid of an excessive free stateit is suitable for high capacity-ization and there are also few liquid spills.

[0017]

[Embodiment of the Invention]The lithium secondary battery of this invention according to claim 1The anode which uses a lithium cobalt oxide as main positive active materialand the negative electrode which used natural graphite or an artificial graphite as main negative electrode active materialIn [have a porous poly membrane arranged among themand nonaqueous electrolyteand] the lithium secondary battery of 400 or more Wh/L volume capacity densityWhen said nonaqueous electrolyte sets the all amount of electrolysis solutions in a cell to QQ Said anodesaid negative electrodeand all the holes Vx of said poly membranelt is expressed by the space between the side of a group and the cell case wall which consist of between said electrode and said poly membrane and said electrodeand said poly membraneand the opening Vy in a cell (the upper part and the lower part of a group)and is $\leq (Vx+0.4Vy)$ $Q \leq (Vx+0.8Vy)$.

***** -- it is characterized by things.

[0018]In the cell of this inventionthe high capacity lithium cobalt oxide is used as the main active material for the anode by high tension for high-capacity-izing.

[0019]Also about the negative electrode of this inventionirreversible capacity is small and is using the high capacity natural graphite or artificial graphite as main negative electrode active material.

[0020]Although it may be conventionally publicly known about the porous poly

membrane used as a separatorpolyethylene with sufficient safetyetc. are used with a thin shape.

[0021]About nonaqueous electrolyteas a nonaqueous solventcyclic carbonatedimethyl carbonate (DMC)such as ethylene carbonate (EC) and propylene carbonate (PC)What mixed two or more sorts of chain carbonatesuch as diethyl carbonate (DEC) and ethyl methyl carbonate (EMC)is preferred. The electrolyte salt can use conventionally publicly known lithium saltsuch as LiPF₆ and LiBF₄.

[0022]As opposed to the space between the side of a group and the cell case wall which consist of between said electrode and said poly membrane and said electrodeand said poly membrane to the total amount Q of electrolysis solutions in this inventionand the opening Vy in a cell (the upper part and the lower part of a group)High capacity and a high lifetime lithium secondary battery can be obtained by specifying the amount of electrolysis solutions. From (Vx+0.4Vy)all the electrolysis solutions Q cannot carry out the water addition of the liquid absorption according [a cell] that it is smallness to expansion of the group of electrode at the time of charge-and-discharge *****but start ***** here. The liquid of the free state which does not participate that it is size in charge and discharge increases in number more than (Vx+0.8Vy)and the danger of a liquid spill becomes large in a top unsuitable to high-capacity-izing.

[0023]The lithium secondary battery of this invention according to claim 2In the lithium secondary battery according to claim 1volume of V2 and said poly membrane is set [the volume of said anode] to V3 for the volume of V1 and said negative electrodeWhen the void content of beta 2 and said poly membrane is set [the void content of said anode] to beta 3 for the void content of beta 1 and said negative electrodeThe group space volume Vx which is said anodesaid negative electrodeand the total hole volume of said poly membrane was calculated by $Vx=V1\beta_1+V2\beta_2+V3\beta_3$ and the electrolysis solution has permeated said group space volume Vx.

[0024]This reason requires that the charging and discharging characteristic in a

cell should originate in the sufficiency state of the electrolysis solution in a power generation element and enough electrolysis solutions should fulfill the hole of an electrode and the hole of a poly membrane. If the electrolysis solution is sufficient the motility about the speed of transfer of the lithium ion to which the anode and the negative electrode passed the separator and the charge transfer between the particles in an electrode i.e. diffusion of a lithium ion will become good.

[0025] As for the colony product V_g in this case it is preferred to occupy not less than 90% of cell inner space in the high capacity cell exceeding 400 Wh/L at the point of stuffing a power generation element as much as possible in a cell.

[0026] At this time the void content beta 1 of said anode and the void content beta 2 of said negative electrode are not less than 10% of 50% or less in the value measured by the mercury porosimeter and it is preferred that it is also not less than 30% of 50% or less in the value by which the void content beta 3 of said poly membrane was measured with the mercury porosimeter.

[0027] When beta 1 and beta 2 will be less than 10% its circumference of liquid is bad and if this reason exceeds 50% it is unsuitable to high-capacity-izing. When beta 3 worsens and a high charging and discharging characteristic exceeds 50% in less than 30% it becomes impossible to maintain safety such as the overcharge characteristic and prevention from an internal short circuit.

[0028] The lithium secondary battery of this invention according to claim 5 In the lithium secondary battery according to claim 1 the space between an electrode and a poly membrane and between the group side and a cell case wall and the opening V_y in a cell (the upper part and the lower part of a group) It is considered as the cell inner space V_{cell} and when volume of the lead which is a member which exists in a cell a tape and a frame is set to **** it is $V_y = V_{cell} - V_g - ***$ and an electrolysis solution is sufficient to said opening V_y . The reason for having specified the electrolysis solution which fills the space between said electrode and said poly membrane and between the group side and a cell case wall and the opening V_y in a cell (the upper part and the lower part of a group) is as follows.

[0029]Although there is almost no design top crevice between an electrode and a poly membranewhen making an electrolysis solution permeate each power generation elementit is thought that it passes along that crevice a little. It is thought that the crevice between a group and a cell wall also has a relation which carries out complementary. If an electrolysis solution does not exist in these crevicesspace will be made between an electrode and said poly membraneand diffusion of the lithium ion in high charge and discharge will be checked. Thereforeit is required for the space between an electrode and said poly membraneand the space between the group-of-electrode side and a cell case wall for the electrolysis solution to be sufficient.

[0030]Although it is an electrolysis solution which exists in the opening in a cell which exists in the upper part and lower space used as a power generation elementin order to make a good charging and discharging characteristic hold in a cellit is necessary to make an electrolysis solution exist also in the space used as the above-mentioned power generation element. As for thispositive active material and negative electrode active material repeat expansion contraction of volume in transfer of a lithium ionand the space in a cell needs to make sufficiency of an electrolysis solution hold to the opening in a cell (the upper part and the lower part of a group)in order to hold the humidity in a systemsince it changes slightly.

[0031]If an electrolysis solution becomes larger than 0.8 of the space between said electrode and said poly membrane and between the group side and a cell case walland the opening Vy in a cell (the upper part and the lower part of a group)the liquid of the free state which does not participate in charge and discharge will increase in numberand the danger of a liquid spill will become large in a top unsuitable to high-capacity-izing.

[0032]In the lithium secondary battery according to any one of claims 1 to 5the viscosity of said electrolysis solution is 5 or less cp of 0.5 or more cpand the angle of contact theta over said anodea negative electrodeand a polymers membrane surface makes the lithium secondary battery of this invention

according to claim 6 $0 < \theta < 80$ degrees.

[0033] If viscosity exceeds 5 cP it will become difficult to satisfy liquid to the hole in a polar plate. At less than 0.5 cP in respect of sufficiency of an electrolysis solution although it is satisfactory conductivity becomes low substantially and a battery characteristic falls.

[0034] Even if viscosity is within the limits of the above when an angle of contact will be not less than 80 **sufficiency into a hole changes difficult.

[0035] It is preferred that the lithium salt which is dissolving into the solvent of an electrolysis solution from a point of a battery characteristic in this case is 2.0 or less mol/l of 0.5 or more mol/l.

[0036]

[Example]<Experiment 1> drawing 1 shows the composition of the lithium secondary battery sealed by the armor body which consists of a metallic material of this invention. As for the fine porous membrane made from polyethylene and 4 in drawing 1a negative electrode lead and 6 are frames a positive electrode lead and 5 as a poly membrane for which 1 separates an anode 2 separates a negative electrode and 3 separates an anode and a negative electrode. The poly membrane 3 the negative electrode 2 and the anode 1 are eventually accommodated in the cell case 7 in the form where lamination winding of the whole was carried out. The inside of a cell is sealed with this obturation board 8.

[0037] The manufacturing method of the power generation element of this cell is explained. After the anode 1 mixed and pasted PVDF which is acetylene black and the binder which are conducting agents to positive-active-material LiCoO₂ it applied this to the charge collector made from Al foil and cut and obtained it in the predetermined size after dry rolling. The positive electrode lead 4 was welded to this anode 1 at the end of the charge collector.

[0038] After the negative electrode 2 mixed and pasted **** to the subject's graphite powder with carboxymethyl cellulose and the binder which are thickeners it was applied to the charge collector made from Cu foil and was cut and obtained in the predetermined size after dry rolling. The negative electrode

lead 5 was welded to this negative electrode 2 at the end of the charge collector. [0039]3 is fine porous membrane made from polyethylene which makes the separator which is a poly membrane and which is usually marketed. Between the above-mentioned anode 1 and the negative electrode 2 the fine porous membrane 3 was piled up together and has been arranged and it wound in the shape of [as shown in drawing 1] an ellipse.

[0040]After storing the wound above-mentioned power generation element the tip part of the positive electrode lead 4 and the negative electrode lead 5 inserted in the armor body 8 (30485 sizes) in the state where it projected outside. The tension rate of the group inserted here was made into 92% from the ratio of total of a polar-plate cross-section area and a separator cross-section area and a battery armor inside-of-the-body cross-section area.

[0041]After pouring in the electrolysis solution of the specified quantity from the opening of the armor body 8 of the cell by which the power generation element was accommodated the obturation board 9 is obturated and a cell is completed. The electrolysis solution used what dissolved LiPF₆ in the solvent which mixed EC and EMC by the volume ratio 1:1 by the concentration of 1 mol/l.

[0042]Design capacity in this cell was set to 800mAh.

[0043]The void content was first calculated for the hole volume in a polar plate from a mixture part-bodies product the true density of a mixture ingredient and a weight ratio and **** volume was drawn. In this example the volume of the anode was 2.00 cc and the mixture part-bodies product was 1.73 cc. The void content of measurement by the mercury porosimeter to a positive electrode mixture part is 20% and hole volume was set to 0.35 cc.

[0044]the volume of a negative electrode is 2.05 cc -- the mixture of a negative electrode -- the volume of the part was 1.89 cc 32% of the void content of the negative electrode mixture part was obtained by measurement of the mercury porosimeter and hole volume was computed with 0.58 cc.

[0045]The volume of said poly membrane is 0.56 cc and 36% of the void content was obtained from the measurement result of the mercury porosimeter. Hole

volume was obtained with 0.20 cc from this. Therefore the hole volume of the space in the polar plate in a county and a separator was obtained with 1.13 cc.

[0046] Between said electrode and said poly membrane. And in the space between the group side and a cell case wall and the opening Vy in a cell (the upper part and the lower part of a group) the cell inner space Vcell was obtained from 5.92 cca volume of 0.17 cc of a cell inner material and the volume of the above-mentioned anode the volume of the above-mentioned negative electrode and the volume of the separator with 1.14 cc.

[0047] It depends The amount of electrolysis solutions of total of the amount of electrolysis solutions with the 0.4 to 0.8 time as much range as space [between hole volume Vx1.13cc of the space in the polar plate in a county and a separators said electrode and said poly membrane and between the group side and a cell case wall] and opening (upper part and the lower part of group) Vy1.14cc in a cell is adjusted As shown in (Table 1) it poured in in the cell and it was considered as cell A-D.

[0048] Amount of electrolysis solutions 3.0 cc/Ah was also adopted with the composition which specifies the amount of electrolysis solutions per cell capacity and it could be 2.4 cc from cell capacity 800mAh. This cell was used as the cell E. However it could not pour in in the cell in practice and the cell was not able to be produced.

[0049] [Charge-and-discharge cycle test] Charging and discharging measurement was performed for these cells under environment with a room temperature of 20 ** again.

[0050] The result of an example is summarized in Table 1 and shown.

[0051]

[Table 1]

[0052] As shown in Table 1Q the all amount of electrolysis solutions in a cell Said anodes said negative electrode and all the holes Vx of said poly membrane it is the

space between the side of a group and the cell case wall which consist of between said electrode and said poly membrane and said electrode and said poly membrane and the opening Vy in a cell (the upper part and the lower part of a group) and is $\leq (Vx + 0.4Vy)$ $Q \leq (Vx + 0.8Vy)$.

The good charging and discharging characteristic was acquired by making the electrolysis solution in which a ** type is realized hold in a cell.

[0053]The capacity deterioration according to shortage of the amount of electrolysis solutions with the cell A is remarkable. In the cell D although a capacity maintenance rate is good since there are many useless electrolysis solutions and there is possibility of a liquid spill as an amount of electrolysis solutions it is not suitable.

[0054]The amount of electrolysis solutions shall be 2.00 cc using the cell of the same composition as the <experiment 2> [electrolysis solution Nakashio concentration examination] experiment 1 for electrolysis solution Nakashio concentration examination. Lithium salt concentration was poured in as 0.4 mol/l/0.5 mol/l/1.0 mol/l/1.5 mol/l/2.0 mol/l and 2.5 mol/l and the cell was constituted. These cells were made into the order of the above-mentioned lithium salt concentration with cell F-K. These cells were carried out on the completely same conditions as the charging and discharging measurement of Example 1.

[0055]The result of Example 2 is summarized in (Table 2) and is shown.

[0056]

[Table 2]

[0057]As shown in (Table 2) cell G-J has a high capacity maintenance rate. It was checked that diffusion of a lithium ion will worsen if salt concentration is low and the viscosity of an electrolysis solution goes up and a charging and discharging characteristic will worsen since the perviousness of an electrolysis solution is bad if ion concentration is high. The viscosity at this time was 5 or more cp.

Measurement of the viscosity in the invention in this application was performed

using the measuring method of JIS K717.

[0058]Although the void content of the separator was made into 41% in this examplethe void content was able to acquire the same effect as this example in 50% or less of range not less than 30%.

[0059]

[Effect of the Invention]By specifying the amount of electrolysis solutionsand the lithium salt concentration contained in itthe amount of electrolysis solutions suitable for a high-density cell with few openings is shownand high capacity and the high lifetime characteristic can be secured from the above thing. This invention can provide the rechargeable lithium-ion battery which has the outstanding charging and discharging characteristic from both this point.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1]Drawing of longitudinal section of the lithium secondary battery of this invention

[Description of Notations]

1 Anode

2 Negative electrode

3 Fine porous membrane made from polyethylene

4 Positive electrode lead

5 Negative electrode lead

6 Frame

7 Case

8 Obturation board

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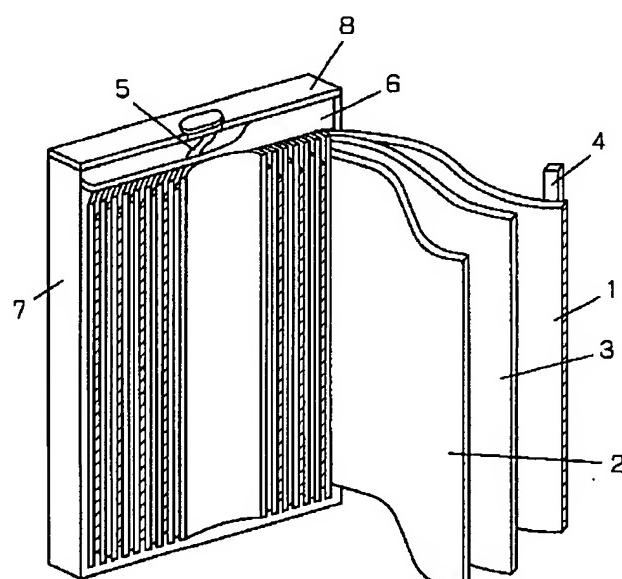
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(54)【発明の名称】 リチウム二次電池

(57)【要約】

【課題】 リチウムイオン二次電池は、400Wh/Lを超える高容量化によって従来の技術での電解液量構成では不適合となる。

【解決手段】 非水電解液は電池内全電解液量をQとした時、Qはリチウムコバルト酸化物を主たる正極活物質とする正極、黒鉛を主たる負極活物質とした負極および前記高分子膜の全空孔Vxと、前記電極と前記高分子膜間および前記電極と前記高分子膜とからなる群の側面と電池ケース内壁との間の空間及び電池内空隙(群の上部および下部)Vyによって表わされ、(Vx+0.4Vy) ≤ Q ≤ (Vx+0.8Vy) が成り立つ。



【特許請求の範囲】

【請求項1】 リチウムコバルト酸化物を主たる正極活物質とする正極と、天然黒鉛または人造黒鉛を主たる負極活物質とした負極と、それらの間に配置された多孔性高分子膜と、非水電解液を備え、かつ体積容量密度が400Wh/L以上のリチウム二次電池において、前記非水電解液は電池内全電解液量をQとした時、Qは前記正極、前記負極及び前記高分子膜の全空孔Vxと、前記電極と前記高分子膜間の空間及び前記電極と前記高分子膜とからなる極板群の側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）の総和Vyによって表わされ、

$$(Vx + 0.4Vy) \leq Q \leq (Vx + 0.8Vy)$$

が成り立つことを特徴とするリチウム二次電池。

【請求項2】 前記正極の体積をV1、前記負極の体積をV2、前記高分子膜の体積をV3とし、前記正極の空孔率をβ1、前記負極の空孔率をβ2、前記高分子膜の空孔率をβ3とした時、前記正極、前記負極および前記高分子膜の全空孔体積である群空間体積Vxが

$$Vx = V1\beta1 + V2\beta2 + V3\beta3$$

で計算され、前記群空間体積Vxに前記電解液が浸透していることを特徴とする請求項1記載のリチウム二次電池。

【請求項3】 極板群の空孔も含めた体積をVgとした時、Vgが電池内空間の90%以上を占有していることを特徴とする請求項2記載のリチウム二次電池。

【請求項4】 前記正極の空孔率β1および前記負極の空孔率β2は水銀ポロシメーターによって測定された値で10%以上50%以下であって前記高分子膜の空孔率β3が水銀ポロシメーターによって測定された値で30%以上50%以下であることを特徴とする請求項2記載のリチウム二次電池。

【請求項5】 前記電極と前記高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）Vyは、電池内空間Vcellとし、電池内に存在する部材であるリード、テープおよび枠体の体積をVpとした時、

$$Vy = V_{cell} - Vg - Vp$$

であることを特徴とする請求項1記載のリチウム二次電池。

【請求項6】 前記電解液の粘度が0.5cp以上5cp以下であって、前記正極、負極および高分子膜表面に対しての接触角θが0<θ<80°である請求項1から5のいずれかに記載のリチウム二次電池。

【請求項7】 前記電解液の溶媒内に溶解しているリチウム塩が0.5mol/l以上2.0mol/l以下であることを特徴とする請求項6記載のリチウム二次電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、リチウム二次電池の電池内電解液の分配量および特性を好適にすることにより電池特性、特にサイクル特性を改善した高容量化リチウム二次電池に関するものである。

【0002】

【従来の技術】 リチウム二次電池の充放電特性やサイクル特性は、正極および負極の活物質種、電解液種などに大きく左右され、さらに、正極および負極の組み合わせ、電解液の電解液量と空隙の関係なども重要な要素となる。

【0003】 リチウム二次電池における電解液の液量規定として、電池容量1Ah当たりの電解液量を規定して電池を構成することにより優れた充放電特性を有するリチウム二次電池を得ることが提案されている（特開平9-231973号公報、特開2000-285959号公報等）。

【0004】 また、積層型電池において、電池内体積あたりの電解液量を規定し、保液率の高いセパレータを用いることによって、発電要素に関与しないフリーの状態（発電要素である正極、負極およびセパレータに浸透していない状態）で存在する電解液の割合を少なくし、電池内圧の上昇による電解液の漏液を押さえるため、セパレータの液保液率を1.5g/cc以上とし、電池内体積あたりの電解液量を0.2cc以上0.4cc未満で電池を構成する構成も提案されている（特開平7-282818号公報）。

【0005】 また、有機焼成体からなる負極を用いたリチウム二次電池において、ガスの内圧上昇を抑制し、内圧上昇による漏液および電池破損等を防止し、長寿命で高信頼性の電池にするため、容器内に容量1Ahあたり0.3cc以上の空隙部を設けることが提案されている（特許第2,646,657号公報）。

【0006】 その他には、リチウムマンガン酸化物からなる正極を用いた非水電解質二次電池において、リチウムの消費量を抑え、容量劣化を抑制するために、正極、負極、およびセパレータそれぞれの空隙率から計算される空隙体積の総和を1としたときに、その非水電解液の液量が、0.8~1.5にすることが提案されている（特開2000-294294号公報）。

【0007】

【発明が解決しようとする課題】 昨今、リチウム二次電池の高容量化が進み、体積容量密度が400Wh/Lを超える電池の研究開発が進められている。

【0008】 この電池の高容量化の技術のひとつとして、極板内の合剤の高密度化および電池内体積にできるだけ発電要素を詰め込むことが進められている。この場合、容量あたりの、発電要素とならない空間はできるだけ少なくする必要があり極板群内の空隙率も小さくなっている。

【0009】 このように、極板群内の空隙率が小さくな

ると容量あたりの液量を規定する方法（特開平9-231973号公報、特開2000-285959号公報等）では、充放電に関与しないフリーの液が多くなり、高容量化に適していない。

【0010】逆に、特開平7-282818号公報に記載の構成のように高い保液率のセパレータを使うことによってフリーの状態を無くす提案もされているが、高容量化電池では、セパレータも薄くて空孔率の低いものを使わざるを得ず、適用することはできない。

【0011】また、特許第2,646,657号公報記載の容器内に容量1Ahあたり0.3cc以上の空隙部を設ける構成は、負極が有機焼成体の場合は有効であるが、高容量化電池では、負極活物質も高容量化のために不可逆容量の小さい黒鉛系の材料を使わざるを得ず、適用することができない。

【0012】さらに、特開2000-294294号公報記載の正極、負極、およびセパレータそれぞれの空隙率から計算される空隙体積の総和を1としたときに、その非水電解液の液量が、0.8~1.5にする構成は、正極がリチウムマンガン酸化物からなる場合には、リチウムの消費量を抑え、容量劣化を抑制するために有効であるが、高容量化電池では、正極活物質も高容量化のために、放電電圧が高く、重量エネルギー密度も高いリチウムコバルト酸化物を使わざるを得ず、適用することができない。

【0013】このように、電池内の発電要素である正極、負極および高分子膜内の空孔、電極と高分子膜間の空間に最適な粘度であって最適な電解液を浸透させ、電池内に最適な電解液量を構成する技術が十分でないという課題があった。

【0014】以上、本発明はこのような課題を解決するものであり、空隙の少ないリチウム二次電池の高容量かつ高寿命を確保することを目的とし、電解液が正極、負極および高分子膜内の空隙、電極とセパレータとなる高分子膜間の空間を最適に満たすことによって、極板内および極板と高分子膜間のリチウムイオンのイオン伝導性を良好なものとし、発電要素である正極活物質および負極活物質を最大限利用できるリチウム二次電池を提供することができる。

【0015】

【課題を解決するための手段】上記目的を達成するためには、本発明のリチウム二次電池は、前記非水電解液において電池内全電解液量をQとした時、Qは前記正極、前記負極及び前記高分子膜の全空孔Vxと、前記電極と前記高分子膜間及び前記電極と前記高分子膜とからなる極板群の側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）Vyによって表わされ、
 $(Vx + 0.4 Vy) \leq Q \leq (Vx + 0.8 Vy)$

が成り立つことを特徴とする。

【0016】

り、高容量かつ高寿命なリチウム二次電池を得ることができる。本発明の電池では、充放電の繰り返しで電極群が膨張した時でも液枯れが無く、また、余分なフリー状態の液が無いため、高容量化に適し、漏液も少ない。

【0017】

【発明の実施の形態】本発明の請求項1に記載のリチウム二次電池は、リチウムコバルト酸化物を主たる正極活物質とする正極と、天然黒鉛または人造黒鉛を主たる負極活物質とした負極と、それらの間に配置された多孔性高分子膜と、非水電解液を備え、かつ体積容量密度が400Wh/L以上のリチウム二次電池において、前記非水電解液は電池内全電解液量をQとした時、Qは前記正極、前記負極および前記高分子膜の全空孔Vxと、前記電極と前記高分子膜間および前記電極と前記高分子膜とからなる群の側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）Vyによって表わされ、

$$(Vx + 0.4 Vy) \leq Q \leq (Vx + 0.8 Vy)$$

が成り立つことを特徴とする。

【0018】本発明の電池では、高容量化のために正極を、高電圧で高容量なリチウムコバルト酸化物を主たる活物質としている。

【0019】本発明の負極に関しても、不可逆容量が小さく、高容量な天然黒鉛または人造黒鉛を主たる負極活物質としている。

【0020】セパレータとなる多孔性高分子膜に関しては、従来公知のもので良いが、薄型で安全性の良いポリエチレンなどを使用する。

【0021】非水電解質に関しては、非水溶媒としてエチレンカーボネート(EC)やプロピレンカーボネート(PC)等の環状カーボネート類やジメチルカーボネート(DMC)、ジエチルカーボネート(DEC)およびエチルメチルカーボネート(EMC)などの鎖状カーボネート類の2種以上を混合したものが好ましい。また、電解質塩はLiPF6やLiBF4など従来公知のリチウム塩が使える。

【0022】本発明においては全電解液量Qに対し、前記電極と前記高分子膜間及び前記電極と前記高分子膜とからなる群の側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）Vyに対し、電解液量を規定することにより高容量かつ高寿命なリチウム二次電池を得ることができる。ここで全電解液Qが(Vx + 0.4 Vy)よりも小であると電池が充放電繰り返したときの極板群の膨張による液吸収を補液することができず液枯れを起こす。また、(Vx + 0.8 Vy)よりも大であると充放電に関与しないフリー状態の液が多くなり、高容量化に不適である上に漏液の危険性が大きくなる。

【0023】本発明の請求項2に記載のリチウム二次電池は、請求項1に記載のリチウム二次電池

正極の体積をV₁、前記負極の体積をV₂、前記高分子膜の体積をV₃とし、前記正極の空孔率をβ₁、前記負極の空孔率をβ₂、前記高分子膜の空孔率をβ₃とした時、前記正極、前記負極および前記高分子膜の全空孔体積である群空間体積V_xが

$$V_x = V_1 \beta_1 + V_2 \beta_2 + V_3 \beta_3$$

で計算され、前記群空間体積V_xに電解液が浸透しているものである。

【0024】この理由は、電池における充放電特性は発電要素内の電解液の充足状態に起因し、十分な電解液が電極の空孔、高分子膜の空孔を満たすことが必要である。電解液が充足しておれば、正極と負極がセパレータを介したリチウムイオンの授受と電極内の粒子間での電荷移動の速度、すなわちリチウムイオンの拡散に関する運動性が良好になる。

【0025】なお、この際、400 Wh/Lを超える高容量電池では、群体積V_gは、電池内空間の90%以上を占有するのが、発電要素を電池内にできるだけ詰め込むという点で好ましい。

【0026】また、この時、前記正極の空孔率β₁および前記負極の空孔率β₂は水銀ポロシメーターによって測定された値で10%以上50%以下であって前記高分子膜の空孔率β₃が水銀ポロシメーターによって測定された値で30%以上50%以下であるのも好ましい。

【0027】この理由は、β₁およびβ₂が、10%未満になると液回りが悪く、また、50%を超えると高容量化に不適である。さらに、β₃が30%未満では、高率充放電特性が悪くなり、50%を超えると過充電特性や内部短絡防止などの安全性が保てなくなる。

【0028】本発明の請求項5に記載のリチウム二次電池は、請求項1記載のリチウム二次電池において、電極と高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_yは、電池内空間V_{c e l l}とし、電池内に存在する部材であるリード、テープおよび枠体の体積をV_pとした時、

$$V_y = V_{c e l l} - V_g - V_p$$

であって、前記空隙V_yに電解液が充足したものである。前記電極と前記高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_yを満たす電解液を規定した理由は以下の通りである。

【0029】電極と高分子膜の間において設計上隙間はほとんどないが、それぞれの発電要素に電解液を浸透させる場合、幾つかの隙間を通っていると考えられる。また、群と電池内壁との間の隙間も相補する関係にあると考えられる。またこれらの隙間に電解液が存在しないと電極と前記高分子膜の間に空間ができてしまい、高率充放電でのリチウムイオンの拡散が阻害される。よって、電極と前記高分子膜間の空間及び極板群側面と電池ケーフ内壁との間の空間に電解液が存在しない時はアレルギー

である。

【0030】また、発電要素とならない上部および下部空間に存在する電池内空隙に存在する電解液であるが電池内に良好な充放電特性を保持させるためには上記発電要素とならない空間にも電解液を存在させておく必要がある。これは、正極活物質および負極活物質がリチウムイオンの授受で体積の膨張収縮を繰り返し、電池内の空間はわずかに変動するので系内の潤滑を保持するためには電池内空隙（群の上部および下部）に電解液の充足を保持させる必要がある。

【0031】また、電解液が前記電極と前記高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_yの0.8より大きくなると充放電に関与しないフリー状態の液が多くなり、高容量化に不適である上に漏液の危険性が大きくなる。

【0032】本発明の請求項6に記載のリチウム二次電池は、請求項1から5のいずれかに記載のリチウム二次電池において、前記電解液の粘度が0.5 cP以上5 cP以下であって、前記正極、負極および高分子膜表面に対しての接触角θが0<θ<80°としたものである。

【0033】粘度が5 cPを超えると極板内の空孔に液が充足しにくくなる。また、0.5 cP未満では、電解液の充足という点では問題がないが、実質的に導電率が低くなり、電池特性が低下する。

【0034】さらに、粘度が上記の範囲内であっても、接触角が80°C以上になると、空孔内への充足が困難になる。

【0035】なお、この場合、電池特性の点から、電解液の溶媒内に溶解しているリチウム塩が0.5 mol/l以上2.0 mol/l以下であることが好ましい。

【0036】

【実施例】<実験1>図1は本発明の金属材料からなる外装体で密封したリチウム二次電池の構成を示す。図1において、1は正極、2は負極、3は正極と負極を隔てる高分子膜としてポリエチレン製微多孔膜、4は正極リード、5は負極リード、6は枠体である。高分子膜3、負極2および正極1は、最終的には全体が積層巻きされた形で電池ケース7内に収容されている。また、この封口板8によって電池内部を密閉する。

【0037】この電池の発電要素の作製方法について説明する。正極1は、正極活物質LiCoO₂に導電剤であるアセチレンブラックと結合剤であるPVDFを混合しペースト化した後、これをAl箔製集電体に塗布し、乾燥圧延の後、所定の大きさに切断して得た。この正極1には正極リード4を集電体の端部に溶接した。

【0038】負極2は、主体の黒鉛粉末に増粘剤であるカルボキシメチルセルロースと結合剤であるを混合してペースト化した後、Cu箔製集電体に塗布し、乾燥圧延の後、所定の大きさに切断して得た。この負極2には負極リード5を集電体の端部に溶接した。

【0039】3は、高分子膜であるセパレータをなす通常市販されているポリエチレン製微多孔膜である。上記の正極1と負極2の間に、微多孔膜3と一緒に重ね合わせて配置し、図1に示すような楕円状に捲回した。

【0040】上記の捲回された発電要素を収納した後、正極リード4と負極リード5の先端部が外部に突出した状態で外装体8（30485サイズ）に挿入した。ここで挿入した群の緊迫率は極板断面積とセパレータ断面積の総和と電池外装体内断面積との比より9.2%とした。

【0041】発電要素が収容された電池の外装体8の開口部から所定量の電解液を注入した後、封口板9を封口して電池を完成させる。電解液はECとEMCを体積比1:1で混合した溶媒にLiPF₆を1mol/lの濃度で溶解したものを用いた。

【0042】また、本電池での設計容量は800mAhとした。

【0043】まず極板中の空孔体積を合剤部体積と合剤成分の真密度と重量比より空孔率を計算し、空効体積を導き出した。本実施例において正極の体積は2.00ccであり、合剤部体積は1.73ccであった。水銀ボロシメーターによる測定から正極合剤部の空孔率は20%であり、空孔体積は0.35ccとなった。

【0044】負極の体積は2.05ccであり、負極の合剤部の体積は1.89ccであり、負極合剤部の空孔率は水銀ボロシメーターの測定によって32%が得られ、空孔体積は0.58ccと算出した。

【0045】また、前記高分子膜の体積は0.56cc

であり、水銀ボロシメーターの測定結果より空孔率36%が得られた。これより空孔体積は0.20ccと得られた。よって、郡内の極板およびセパレータ内の空間の空孔体積は1.13ccと得られた。

【0046】前記電極と前記高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_yは電池内空間V_{cell}は5.92ccと電池内部材の体積0.17ccと上記正極の体積と上記負極の体積およびセパレータの体積から1.14ccと得られた。

【0047】よって、電解液量を郡内の極板およびセパレータ内の空間の空孔体積V_x1.13ccと前記電極と前記高分子膜間および群側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_y1.14ccの0.4~0.8倍の範囲との総和の電解液量を調整し、（表1）に示すように電池内に注液し、電池A~Dとした。

【0048】さらに、電池容量あたりの電解液量を規定する構成で電解液量3.0cc/Ahものを採用し、電池容量800mAhから2.4ccとした。この電池を電池Eとした。しかし、実際は電池内に注液することができず、電池は作製できなかった。

【0049】[充放電サイクル試験] またこれらの電池を室温20°Cの環境下で充放電測定を行った。

【0050】実施例の結果を表1にまとめて示す。

【0051】

【表1】

電池	電解液量yのV _y に対する比	電解液量(cc)	100サイクル時容量維持率(%)
A	0.2	1.36	81
B	0.4	1.59	89
C	0.8	2.04	92
D	1.0	2.27	93

【0052】表1に示すように、電池内全電解液量をQが前記正極、前記負極および前記高分子膜の全空孔V_xと、前記電極と前記高分子膜間および前記電極と前記高分子膜とからなる群の側面と電池ケース内壁との間の空間及び電池内空隙（群の上部および下部）V_yであつて、

(V_x+0.4V_y) ≤ Q ≤ (V_x+0.8V_y) の式が成り立つ電解液を電池内に保持させることで良好な充放電特性が得られた。

【0053】また、電池Aでは、電解液量の不足による容量劣化が著しい。電池Dでは、容量維持率が良いものの無駄な電解液が多く、漏液の可能性があるため電解液量としては適していない。

【0054】<実験2>

[電解液中塩濃度検討] 実験1と同じ構成の電池を用い、電解液中塩濃度検討のために電解液量を2.00ccとして、リチウム塩濃度を0.4mol/l、0.5mol/l、1.0mol/l、1.5mol/l、2.0mol/l、2.5mol/lとして注液して電池を構成した。これらの電池を上記リチウム塩濃度の順に電池F~Kとした。これらの電池を実施例1の充放電測定と全く同じ条件で実施した。

【0055】実施例2の結果を（表2）にまとめて示す。

【0056】

【表2】

電池	塩濃度 (m o l / l)	粘度 (c p)	100サイクル時 容量維持率 (%)
F	0.4	0.4	79
G	0.5	0.5	89
H	1	1.6	93
I	1.5	2.6	92
J	2	3.9	90
K	2.5	5.1	82

【0057】(表2)に示すように、電池G～Jは容量維持率が高い。塩濃度が低いとリチウムイオンの拡散が悪くなり、イオン濃度が高いと電解液の粘度が上がり電解液の浸透性が悪いため充放電特性が悪くなることが確認された。この時の粘度は5 c p以上であった。また、本願発明における粘度の測定はJ I S規格K 717の測定方法を用いて行った。

【0058】また、本実施例ではセパレータの空孔率を41%としたが、空孔率は30%以上50%以下の範囲で本実施例と同様の効果を得ることができた。

【0059】

【発明の効果】以上のことから、電解液量とその中に含まれるリチウム塩濃度を規定することで、空隙の少ない高密度な電池に適した電解液量を示し、高容量かつ高寿

命な特性を確保できる。この両点から本発明は優れた充放電特性を有するリチウムイオン二次電池を提供できるものである。

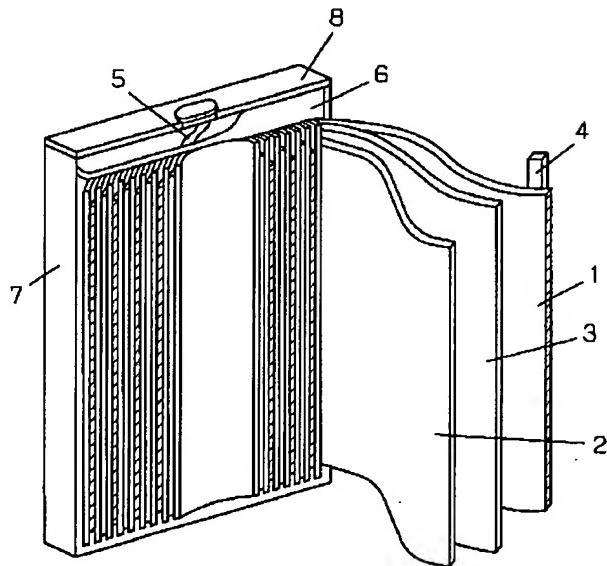
【図面の簡単な説明】

【図1】本発明のリチウム二次電池の縦断面図

【符号の説明】

- 1 正極
- 2 負極
- 3 ポリエチレン製微多孔膜
- 4 正極リード
- 5 負極リード
- 6 枠体
- 7 ケース
- 8 封口板

【図1】



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